

Evaluation of Wetland Methyl Mercury Export as a Function of Experimental Manipulations

Mae Sexauer Gustin,* Prithviraj V. Chavan, Keith E. Dennett, Eric A. Marchand, and Susan Donaldson

ABSTRACT

Mercury associated with natural enrichment, historic mining, and ore processing is a contaminant of concern in watersheds of the western USA. In this region, water is a highly managed resource and wetlands, known to be important sites of methyl mercury production, are often an integral component of watersheds. This study applied controlled manipulations of four replicated experimental wetland designs with different water and soil mercury concentrations to determine the potential impacts on methyl mercury export. Wetlands were manipulated by drying and wetting, changing hydraulic retention time, and adding sulfate and nitrate to influent waters. In a summer drying and wetting manipulation, an immediate increase in total methyl mercury release was observed with rewetting, however, concentrations decreased quickly. Drying all wetlands over the winter and rewetting in the spring resulted in high net methyl mercury output relative to that observed before drying. Net methyl mercury output was not influenced by changes in hydraulic retention time from 4 to 8 h or to 30 min, or by increasing the nitrate concentration from 0.1 to 10 mg L⁻¹. The addition of sulfate to the inlet waters of two mesocosms to increase concentrations from ~100 to 250 mg L⁻¹ did not result in a clear effect on methyl mercury output, most likely due to sulfate concentrations being higher than optimal for methyl mercury production. Despite the lack of response to sulfate amendments, the change in sulfate concentration between the inlet and outlet of the mesocosms and temperature were the parameters best correlated with methyl mercury outputs.

IN THE LAST FEW DECADES wetland construction and restoration has received considerable attention for improving water quality, flood control, habitat for endangered species, and aesthetic values (Dahl, 2000). However, wetlands are potential sites for mercury (Hg) methylation in natural systems due to the anaerobic nature of the wetland environment (Krabbenhoft et al., 1995; Rudd, 1995; Branfireun et al., 1996; Driscoll et al., 1998; Morel et al., 1998; Schwesig et al., 1999). Methyl mercury (MeHg) is of concern because it is bioaccumulated and biomagnified within food chains (Kelly et al., 1995). Demethylation can also occur in wetland environments and may be a reductive or oxidative process (Compeau and Bartha, 1985; Gilmour and Henry, 1991; Oremland et al., 1991; Pak and Bartha, 1998; Mason and Lawrence, 1999; Marvin-DiPasquale and Oremland, 1998). Net methylation is determined by measuring methylation and demethylation simultaneously in the same en-

vironment (Zillioux et al., 1993). With constructed wetlands, the MeHg export can be determined by measuring concentrations in inflow and outflow waters; however, production of MeHg in the sediments may not be equated with output unless it is directly measured.

Steamboat Creek (SBC), Washoe County, Nevada, USA, is a major source of nonpoint N, P, and total suspended solids (TSS) to the Truckee River which ends in a terminal water body (Stamenkovic et al., 2005). The creek has also been documented as having high Hg concentrations in both water and sediments (Lyons et al., 1998; Blum et al., 2001; Thomas, 2003; Stamenkovic et al., 2004). Mercury in the creek water is derived primarily from mine wastes that have been distributed down the creek from the headwaters since the late 1800s (Lyons et al., 1998; Blum et al., 2001; Stamenkovic et al., 2005). The construction of a wetland-flood control system at the confluence of the Truckee River and SBC had been proposed as a component of a regional watershed restoration plan developed by the Washoe County Department of Water Resources and the U.S. Army Corps of Engineers. Ten experimental wetland mesocosms were constructed near the confluence of the creek and the Truckee River at the Truckee Meadows Water Reclamation Facility (TMWRF) in Sparks, Nevada (Spurkland, 2001; Stamenkovic et al., 2005; Gustin et al., 2006) to allow for investigation of the influence of wetland conditions on nutrient and Hg biogeochemical cycling using SBC and TMWRF waters. A discussion of the seasonal trends of total and MeHg outputs associated with the four experimental designs over time are presented in Stamenkovic et al. (2005) and Gustin et al. (2006).

This study focused on manipulation of wetland mesocosms to test the hypotheses that drying and wetting, long hydraulic residence time (HRT), and addition of SO₄²⁻ would stimulate MeHg export; and an increase in NO₃⁻ concentration from 0.1 to 10 mg L⁻¹ would reduce MeHg output. It was thought that these manipulations would provide some insight as to the impacts of western water management on the output of MeHg from wetlands. Drying and rewetting of wetlands and changes in flow regimes are common phenomena in western watersheds due to limited water availability. Chemical manipulations entailed the addition of sulfate and nitrate to wetland influent. It is well established that sulfate-reducing bacteria methylate inorganic Hg (Compeau and Bartha, 1985; Gilmour and Henry, 1991) and the presence of sulfate enhances Hg methylation (Gil-

M. Sexauer Gustin, Dep. of Natural Resources and Environmental Sciences, Univ. of Nevada, Reno, NV 89557. P.V. Chavan, K.E. Dennett, and E.A. Marchand, Dep. of Civil and Environmental Engineering, Univ. of Nevada, Reno, NV 89557. S. Donaldson, Nevada Cooperative Extension, Reno, NV 89520. Received 22 Dec. 2005. *Corresponding author (msg@unr.nevada.edu).

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677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: TSS, total suspended solids; HRT, hydraulic resistance time; ORP, oxidation reduction potential; DO, dissolved oxygen; THg, total mercury; TMWRF, Truckee Meadows Water Reclamation Facility; TOC, total organic carbon; MeHg, methyl mercury; SBC, Steamboat Creek.

mour and Henry, 1991; Gilmour and Riedel, 1995; King et al., 1999; Branfireun et al., 1999; Swain et al., 2004; Bonzongo, 2004). Nitrate additions were done to address the hypothesis of Stamenkovic et al. (2005) who found that MeHg output was greater in the wetland mesocosms with TMWRF waters relative to those with SBC water and suggested that the difference was due to the higher NO_3^- concentrations in SBC water relative to TMWRF water.

MATERIALS AND METHODS

Site Description

This study used 8 of 10 surface flow parallel mesocosms located adjacent to the TMWRF in Sparks, Nevada, USA. Each mesocosm had a 4.5-mm rubber liner, ~0.6- to 1-m-thick soil base, and was divided into three equal length cells of 1.8 m wide and 3 m long. Influent water included that from SBC (25 to 318 ng Hg L^{-1}), referred to as Hg-contaminated water (Fig. 1) and TMWRF treated wastewater (4 to 16 ng Hg L^{-1}), referred to as clean water. Wetland influent waters were first pumped to a head tank from which a controlled flow of water was gravity fed through each wetland mesocosm. Sediments from SBC ($0.86 \pm 0.52 \mu\text{g Hg g}^{-1}$ dry weight, referred to as contaminated sediments) were used for the sediment base for four mesocosms, whereas low Hg substrate or clean substrate, derived from the surrounding area outside of the immediate SBC floodplain ($0.09 \pm 0.03 \mu\text{g Hg g}^{-1}$ dry weight), was used for the others (Fig. 1). Mesocosms were heavily vegetated with ~70% cattails (*Typha* sp.) and rushes (*Juncus* sp.), and duckweed (*Lemna* sp.).

Sample Collection

Unfiltered and filtered water samples were collected from the inflow and outflow of each mesocosm using clean sampling techniques (USEPA Method 1669) and acid-washed Teflon bottles (Keeler et al., 1995). Immediately after collection samples were preserved with optima hydrochloric acid (0.4%)

and refrigerated. Samples were filtered on site using a peristaltic pump, acid-cleaned Teflon tubing, and 0.45- μm Teflon capsule filters (Swico, part # FFC1011PEY). Filter blanks were collected during each sampling using Millipore Milli-Q 18.2 m Ω water in the field. At the time of collection of samples for Hg analyses, water samples were also taken for laboratory analyses of water quality parameters and in situ surface water temperature, pH, and oxidation reduction potential (ORP).

Analytical Methods

Unfiltered methyl Hg (MeHg) and filtered $<0.2 \mu\text{m}$ (MeHg_D) concentrations in water were determined using cold-vapor atomic fluorescence spectrophotometry (CVAFS) after distillation and aqueous phase ethylation, and isothermal GC separation (Bloom, 1989; USEPA Method 1630). Total Hg (THg) concentrations of filtered and unfiltered water samples were determined after bromine monochloride oxidation, stannous chloride reduction, and purging of Hg from solution onto gold-coated quartz sand traps (Bloom and Creclius, 1983). Mercury on the traps was analyzed by dual amalgamation and CVAFS (Dumarey et al., 1985; Bloom and Fitzgerald, 1988; USEPA Method 1631). The analytical detection limits (three standard deviations of method blanks) were 5 pg L^{-1} ($n = 12$) for MeHg and 1 ng L^{-1} ($n = 15$) for THg. Coefficient of variation of triplicate analyses of water for MeHg and THg were $4.0 \pm 2.9\%$ ($n = 74$), and $7.5 \pm 4.5\%$ ($n = 99$), respectively. Bottle blanks were $0.8 \pm 0.3 \text{ ng L}^{-1}$ ($n = 26$) for THg and $0.017 \pm 0.008 \text{ ng L}^{-1}$ ($n = 17$) for MeHg. Filter blanks were $0.5 \pm 0.3 \text{ ng L}^{-1}$ ($n = 26$) for THg and $0.012 \pm 0.005 \text{ ng L}^{-1}$ ($n = 17$) for MeHg. Average blank spike and matrix spike recoveries for MeHg in water were $118 \pm 18\%$ ($n = 13$) and $101 \pm 19\%$ ($n = 17$), respectively. Dogfish muscle standard (National Research Council Canada, DORM-2) dissolved in 0.5% KOH methanol solution was used for MeHg quality assurance and measured concentrations were $119 \pm 5\%$ ($n = 73$) of the certified value.

Nitrogen and phosphorus species, TSS, SO_4^{2-} , dissolved oxygen (DO), and total organic carbon (TOC) were analyzed

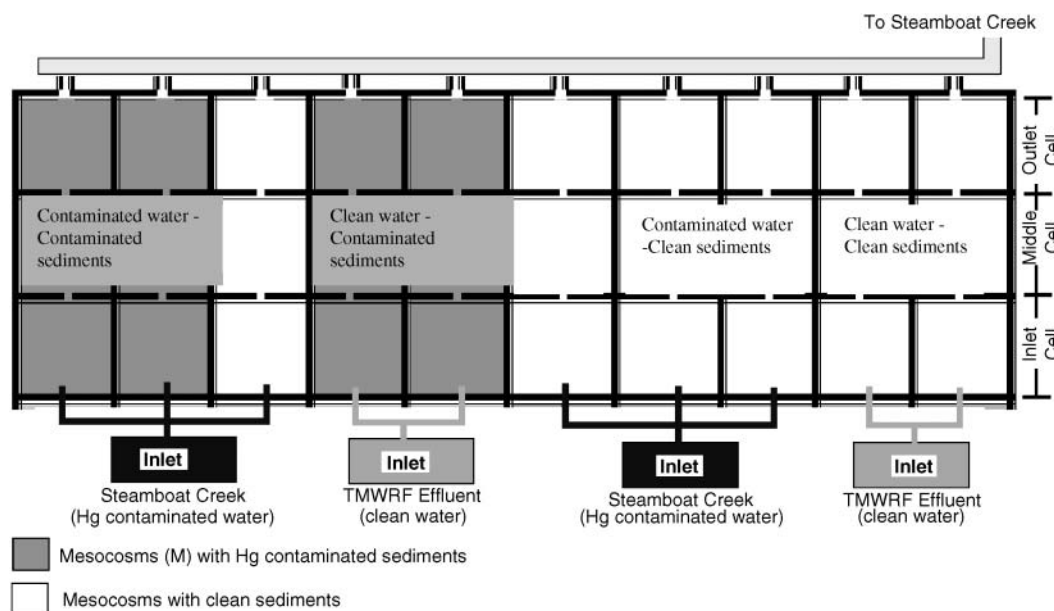


Fig. 1. Schematic showing the experimental designs for constructed wetland mesocosms used for this study. Paired mesocosms used for the manipulations are indicated by common labeling. In most cases one of the paired mesocosms was used as a control and the other manipulated.

following protocols in the Standard Methods for the Examination of Water and Wastewater (APHA, 1995) (cf. Stamenkovic et al., 2005). Temperature and pH were measured using YSI, Model 30, and Orion Instruments, Model 290A, respectively. Oxidation-reduction potential in the water column was measured using a platinum electrode and Ag/AgCl reference electrode connected to a pH meter (Orion Instruments, Model 290A) (Faulkner et al., 1989).

Wetland Manipulations

For each manipulation, except the seasonal drying experiment (winter to spring dry and spring re-wetting), a replicate set of mesocosms were used with one as the control (labeled CM) and the other manipulated (labeled MM). Mesocosms with Hg-contaminated sediments were used for the summer drying and wetting experiment (5 Aug. 2003 to 30 Sept. 2003). In this experiment continuous water flow was maintained in the control mesocosms, whereas for the manipulated mesocosms water flow was stopped (~50 d) and the wetlands allowed to dry until the soil moisture was <10%, then flow was resumed. Filtered and unfiltered samples were collected 2 d before terminating water flow into manipulated mesocosms and every day for 5 d after flow resumed.

In a wetting and drying experiment simulating seasonal winter drying and spring rewetting, flow was turned off to all wetland mesocosms from February to May 2004. Water samples were collected just before drying. In the beginning of May, the flow was turned on for 4 d and then off and the mesocosms were allowed to dry again for 1 wk. This cycle was repeated and afterward water input to all wetlands remained on and water samples were collected every other day for 6 d and at 50 d.

For the HRT experiments, mesocosms receiving Hg-contaminated water with contaminated sediments and clean sediments were used. The standard HRT for all wetland mesocosms was 3.5 ± 0.5 h. For one manipulation retention time was increased to 7.5 ± 0.5 h for 27 d (5 July 2004 through 5 Aug. 2004). Water samples were collected 1 d before increasing the HRT, at Days 9, 18, and 27 during the manipulation, and 1 wk after the retention time had been returned to 3.5 h. After 1 mo, the retention time for the same mesocosms was decreased to 30 ± 5 min. Water samples were collected 1 d before decreasing the HRT (8 Sept. 2004 through 5 Nov. 2004), at Days 11, 20, and 46 during the manipulation, and 1 wk after returning to the 3.5 h retention time.

For the SO_4^{2-} and NO_3^- addition experiments, mesocosms with clean water, Hg-contaminated sediments, and clean sediments were used. For both, samples were collected 1 d before the addition. Sulfate as sodium sulfate (Na_2SO_4) was continuously added to the influent of the manipulated mesocosms to increase the concentration from 100 ± 10 mg L^{-1} in the TMWRF effluent to 250 ± 10 mg L^{-1} . Samples were taken on Days 9, 18, and 27 during addition, and 7 d after the addition was stopped (5 July 2004 through 5 Aug. 2004). One mo after termination of the SO_4^{2-} experiment (from 8 Sept. 2004 through 5 Nov. 2004) NO_3^- as a potassium nitrate (KNO_3)

solution was continuously added to raise the concentration from 0.1 mg L^{-1} in the TMWRF effluent to 10 mg L^{-1} . Water samples were collected on Days 11, 20, and 46 of NO_3^- addition, and 1 wk after the manipulation was terminated.

All of the statistical analyses were performed using StatView Version 5.0.1 (SAS Inst.).

RESULTS

General Conditions

During these experiments total Hg and methyl Hg concentrations, TSS, and N speciation differed significantly between contaminated vs. clean influent waters (Table 1). Total organic carbon was higher and pH slightly less in the TMWRF waters relative to the SBC water. Temperature of clean water was slightly higher but not significantly different from creek water, ranging from 15 to 27°C, with the highest temperatures during July and August. Based on oxidation-reduction potential (≥ 200 mV) and DO (Table 1) data, both influent waters were well aerated. Since most of the Hg input to the mesocosms in creek water was particulate-bound, wetlands with this source water were a significant sink for total Hg. In contrast, wetlands with clean water and contaminated sediments were predominantly a slight source of total Hg, whereas those with clean water and clean sediments were a slight sink (cf. Stamenkovic et al., 2005; Gustin et al., 2006). No significant differences in total mercury (THg) fluxes for treated and control mesocosms were observed during any of the manipulations.

Drying and Wetting Manipulations

Results of the summer drying and wetting experiment showed that net MeHg outputs from the dried and then rewetted mesocosms were greater than that measured for the mesocosms through which continuous flow was maintained (Fig. 2). After the return of water flow through the dried wetland mesocosms, they became sources of MeHg ($\Delta C = 0.1$ to 0.6 ng L^{-1}), whereas the control mesocosms were net sinks ($\Delta C = -5.8$ to -0.1 ng L^{-1}). After ~3 d of renewed flow ΔC MeHg for the control and manipulated mesocosms became similar. Both manipulated mesocosms became sources of TSS after wetting, whereas the control mesocosms remained a sink (contaminated water) or had low net output (clean water) (Fig. 2).

Before the drying of mesocosms in the seasonal manipulation in which all were dried from late winter to early spring, the systems were either a sink or a slight source ($\Delta C = -0.7$ to 0.2 ng L^{-1}) of MeHg before drying (Fig. 3). After continuous flow was resumed, all

Table 1. Mean \pm standard deviation concentrations for relevant water quality parameters in contaminated or Steamboat Creek water, and clean water or treatment plant effluent: total and methyl mercury concentrations (ng L^{-1}), pH, and average concentration (mg L^{-1}) of dissolved oxygen (DO), inorganic nitrogen ($\text{NO}_3^- + \text{NO}_2^-$), organic nitrogen (as TKN), total phosphorus (TP), orthophosphate (OP), total suspended solids (TSS), and total organic carbon (TOC).

| Influent | THg* | MeHg* | pH | DO | $\text{NO}_3^- + \text{NO}_2^-$ * | TKN | TP | OP | TSS* | TOC |
|----------|---------------|-----------------|---------------|---------------|-----------------------------------|---------------|---------------|-----------------|-------------|---------------|
| SBC | 172 \pm 147 | 4.25 \pm 4.21 | 8.2 \pm 0.4 | 6.7 \pm 3.2 | 0.5 \pm 0.2 | 1.0 \pm 0.4 | 0.5 \pm 0.5 | 0.2 \pm 0.06 | 32 \pm 18 | 4.5 \pm 1.9 |
| TMWRF | 10 \pm 6 | 0.61 \pm 0.59 | 7.6 \pm 0.5 | 5.2 \pm 1.4 | 0.1 \pm 0.1 | 1.9 \pm 0.3 | 0.2 \pm 0.1 | 0.15 \pm 0.05 | 8 \pm 5 | 7.9 \pm 3.2 |

* Paired *t* test indicated significant ($p < 0.05$) differences between SBC and TMWRF water.

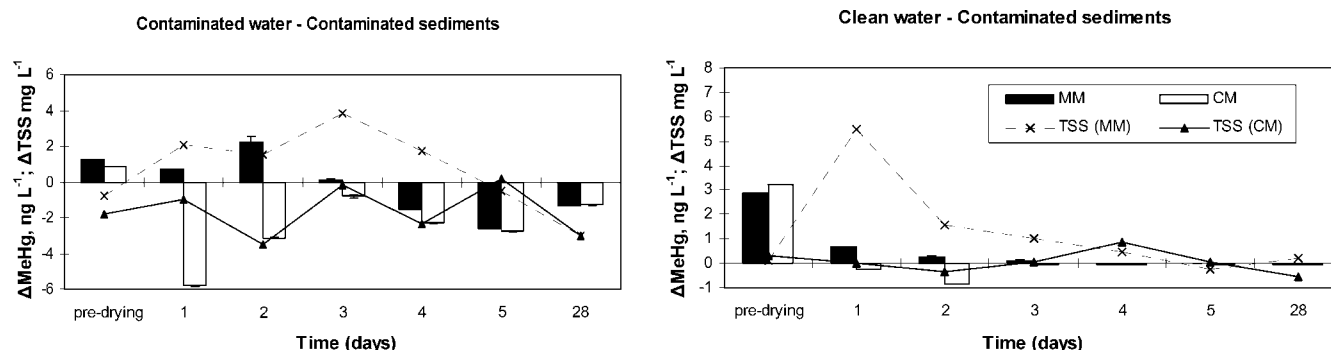


Fig. 2. The $\Delta\text{C MeHg}$ (outlet-inlet concentrations) in water before and after drying and subsequent rewetting. Control mesocosm (CM) indicates data in which flow was maintained over the course of the manipulation and manipulated mesocosm (MM) data for which flow was stopped and the wetlands allowed to dry. The $\Delta\text{C TSS}$ (outlet-inlet) indicates total suspended solids concentration.

mesocosms became a MeHg source (1.7 to 8 ng L⁻¹ for contaminated water and 0.6 to 3.2 ng L⁻¹ for clean water wetlands). The net MeHg output in the contaminated water mesocosms after rewetting was greater than that observed later in the summer and at the same time the previous year ($\Delta\text{C} \sim 1.5$ ng L⁻¹) (cf. Gustin et al., 2006). For the wetlands with clean water, MeHg output concentrations were comparable to those measured later in the summer and in the previous year (1 to 3.2 ng L⁻¹) for those with contaminated sediment, but were greater than that measured at other times for those with clean sediments (< 0.8 ng L⁻¹). In this wetting and drying exercise TSS concentrations did not increase in the outlet waters with the final rewetting.

Changing Hydraulic Retention Time

Increasing the HRT from 3.5 to 8 h in mesocosms with TMWRF influent and both clean and contaminated sediments produced no clear change in $\Delta\text{C MeHg}$ concentrations of the manipulated mesocosms relative to the controls. Similarly, no significant change between manipulated and control mesocosms $\Delta\text{C MeHg}$ concentrations were observed when the HRT was decreased from 4 h to 30 min.

Chemical Manipulations

The $\Delta\text{C MeHg}$ concentrations in mesocosms amended with sulfate were lower than the respective control me-

socosms initially, and remained such or slightly higher through Day 18; however, for samples collected on Day 27 $\Delta\text{C MeHg}$ was higher in the manipulated systems relative to the control mesocosms. One week after the SO_4^{2-} addition terminated, the manipulated mesocosms again had lower $\Delta\text{C MeHg}$ than the control mesocosms. The MeHg output during SO_4^{2-} addition on Day 27 for both manipulated mesocosms increased by a factor of two; however, it was greater for that with contaminated sediments [4 vs. 0.3 ng L⁻¹ (Fig. 4)].

No consistent change in $\Delta\text{C MeHg}$ was observed in NO_3^- -amended mesocosms when compared to the control mesocosms (Fig. 5). The decrease in $\Delta\text{C MeHg}$ on Day 20 of the manipulation in treated and control mesocosms corresponded with a drop in water temperature of 8°C. This manipulation was in the fall when extreme temperature shifts may occur in the study area.

Other Environmental Influences on Methyl Mercury Output

Weak but significant positive correlations between temperature and $\Delta\text{C MeHg}_D$ were calculated for data collected from each experiment ($r^2 = 0.12$ to 0.30 , $p < 0.05$), except for the single drying and wetting experiment. Similarly, weak negative correlations between effluent water ORP vs. $\Delta\text{C MeHg}_D$ were calculated using data from each manipulation ($r^2 = 0.21$ to 0.32 , $p < 0.05$). No correlation was observed between pH and $\Delta\text{C MeHg}_D$ during any of the manipulations, probably due

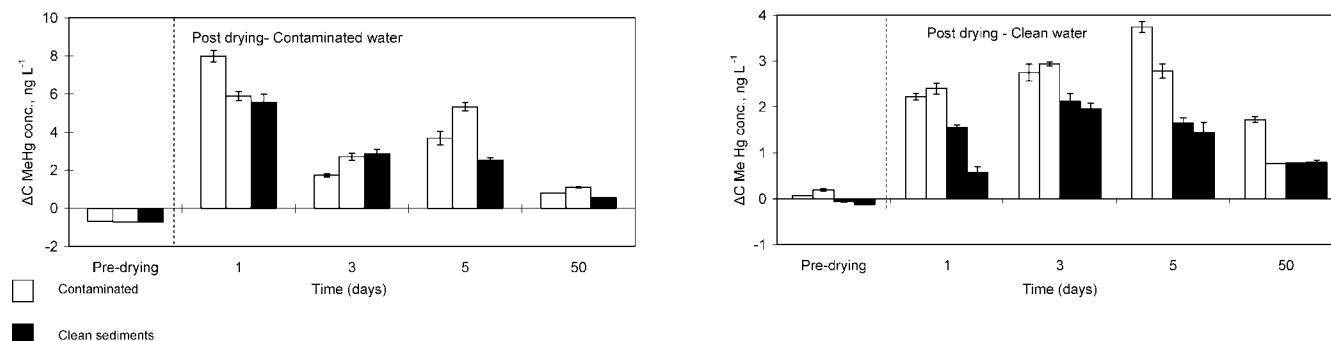


Fig. 3. The $\Delta\text{C MeHg}$ (outlet-inlet) concentration in water before and after drying over the winter and during resumed flow after subsequent rewetting in the spring. The left panel is data from the mesocosms with contaminated water and the right panel from those with clean water. Open bars represent mesocosms with contaminated sediments and those with dark bars represent clean sediments.

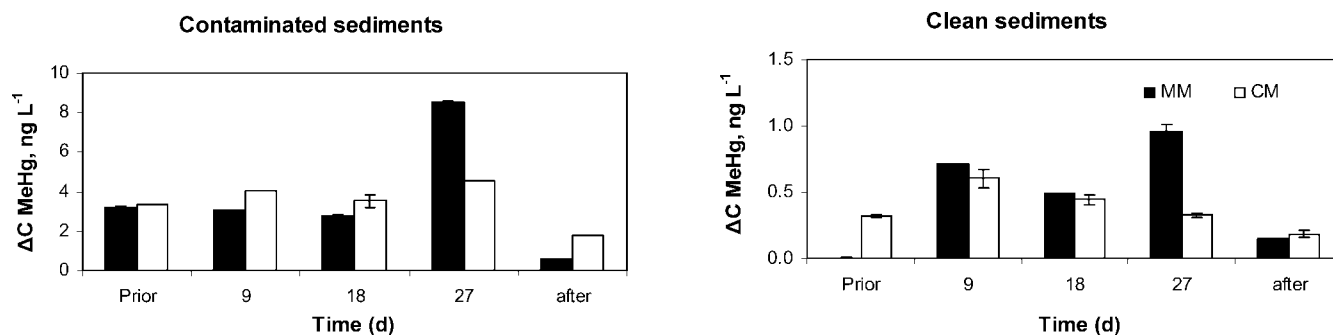


Fig. 4. The ΔC MeHg concentrations in water before, during, and after the sulfate addition. Sulfate was added to mesocosms with clean water influent and Hg-contaminated sediments (left panel) and clean sediments (right panel). CM indicates the control mesocosm, whereas MM indicates data from the manipulated mesocosm.

to the low variation in pH during the study. Similar correlations were found for Δ MeHg_D and ΔC total MeHg concentrations measured in unfiltered waters.

For all experiments outlet water SO_4^{2-} concentrations were always lower than associated inlet waters [ΔC SO_4^{2-} (inlet minus outlet concentration) = 17.6 ± 13.5 mg L⁻¹], indicating that SO_4^{2-} was being removed as the water flowed through the wetlands. Overall the manipulations ΔC SO_4^{2-} vs. ΔC MeHg_D concentrations were correlated ($r^2 = 0.41$, $p < 0.05$) (Fig. 6).

DISCUSSION

General

Total Hg fluxes were not influenced by any experimental treatments performed during this study. In general, the wetland mesocosms receiving Hg-contaminated water functioned as a sink for THg (-2 to -120 $\mu\text{g m}^{-2} \text{d}^{-1}$) and those with clean water (-3.1 to 17 $\mu\text{g m}^{-2} \text{d}^{-1}$) acted as sink for THg when clean sediments were the substrate, and a slight source or sink when contaminated sediments were used. The first trend can be attributed to deposition of particulate-bound Hg from creek water as the velocity decreased when entering the wetlands (cf. Stamenkovic et al., 2005).

Manipulations

In both the summer and seasonal drying and wetting manipulations, MeHg output increased with rewetting. In the summer drying and wetting experiment the increased MeHg output was short-lived and correlated

with an increase in TSS. Because of this increased MeHg, export after rewetting is thought to be due to the "reservoir effect," described as the flushing of MeHg-bound to fine particulates as flow resumes in wetlands that have dried (Cox et al., 1979; Bodaly et al., 1997).

After the winter drying and spring rewetting (several times) of all wetlands (seasonal drying and wetting manipulation) an exacerbated flux was observed in the wetlands with contaminated water-contaminated sediments and clean water-clean sediments relative to other similar times the previous year and to later in the summer. The output in the mesocosms with clean water and contaminated sediments was similar to data collected the previous year. Additionally, an increase in TSS of the effluent waters relative to the samples taken before the drying was not observed. The lack of increase in TSS may be due to the finer material that would have been deposited at the sediment-water interface, having been flushed out during the first and second drying and rewetting cycles.

A seasonal trend of higher MeHg output during the warmer months has been documented for the mesocosms with contaminated sediments (Stamenkovic et al., 2005; Gustin et al., 2006). The exacerbated MeHg output during the spring rewetting relative to that observed in previous years may be due to resumed water flow indirectly affecting flux by impacting wetland processes that influence MeHg production. For example, Gilmour et al. (2005) showed, based on laboratory studies, that rewetting of soils stimulated MeHg production by increasing sulfate availability through oxidation of sulfide. Additionally, the drying was initiated in February, when

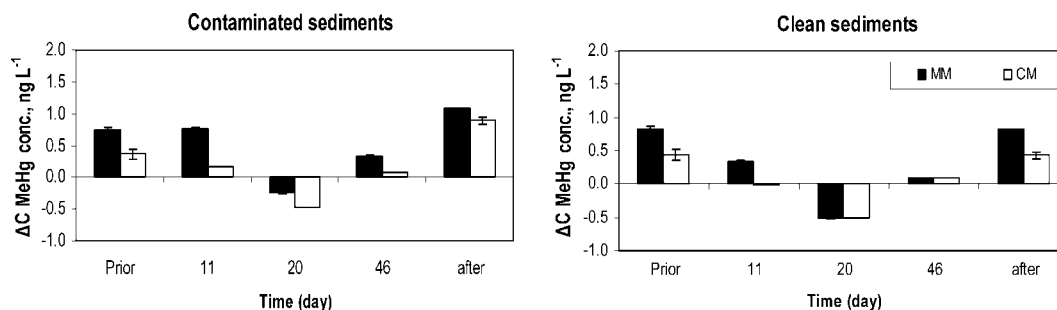


Fig. 5. The ΔC MeHg in water between the mesocosm outlet and inlet prior, during, and after (Day 63) nitrate addition for designs with clean water and Hg-contaminated sediments (left side) and clean sediments (right side).

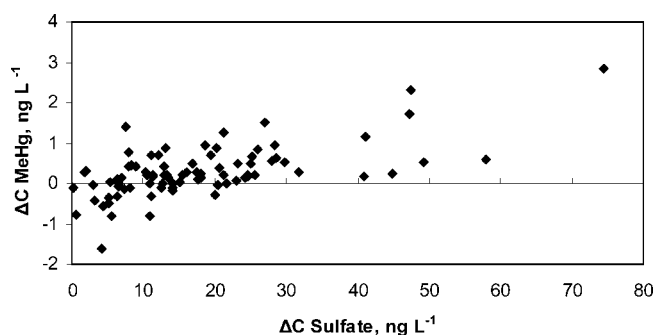


Fig. 6. The ΔC sulfate concentration (inlet minus outlet) and ΔC dissolved methyl mercury (MeHg_D) (outlet minus inlet) concentration for all data collected during this study.

it was cold, and flow resumed in April when water temperatures were $\sim 7^{\circ}\text{C}$ higher. This higher output during warmer temperatures could have been due to enhanced microbial activity that occurs under warmer conditions (cf. Korthals and Winfrey, 1987; Mauro et al., 1999). Alternatively, conditions during resumed flow could have not affected production of MeHg but instead enhanced the release of MeHg from the sediments to the water column.

Changes in HRT resulted in no change in MeHg output. This does not necessarily imply that MeHg production was not influenced, for the system output may not reflect production in the sediments. Wetland conditions could result in an increase in MeHg production and in the pool of MeHg in the wetland sediments; however, if this Hg is not transferred from the sediment to the water, the increased production will not be evident based on differences in concentrations between the inlet and outlet waters.

A twofold increase in ΔC MeHg concentrations was observed for the manipulated mesocosms for data collected the 27th day of sulfate exposure. During the two prior sampling dates there was not a clear difference in ΔC MeHg for the control vs. manipulated mesocosms. The lack of a clear and immediate increase in MeHg output with the sulfate addition may due to the fact that SO_4^{2-} concentrations in the clean water were already greater (~ 80 to 100 mg L^{-1}) than that suggested to be optimal for MeHg production (20 to 50 mg L^{-1} ; Gilmour and Henry, 1991). It is possible that at these sulfate concentrations other parameters that affect MeHg output such as pH, ORP, dissolved organic carbon, and temperature would have a greater influence on MeHg flux (Compeau and Bartha, 1985; Korthals and Winfrey, 1987; Steffan et al., 1988; Gilmour et al., 1992; Heyes et al., 1998; Gilmour et al., 1998; Pak and Bartha, 1998; King et al., 1999; King et al., 2000; Ekstrom et al., 2003).

Despite the fact that there was no immediate effect of increasing sulfate concentrations on the output of MeHg, sulfate consumption or $\Delta C \text{ SO}_4^{2-}$ concentration between the inlet and outlet waters was correlated with $\Delta C \text{ MeHg}_D$ (Fig. 6). The observed decrease in SO_4^{2-} concentrations between the inlet and outlet waters of all mesocosms is hypothesized to be due primarily to consumption by microorganisms during sulfate reduction.

Stamenkovic et al. (2004) reported a sulfate reduction rate of $18 \pm 6 \text{ nmol cm}^{-3} \text{ dry sediment day}^{-1}$, and high pore water reduced sulfur for one of the mesocosms with contaminated water and sediments. Sulfate reduction is an important process in anaerobic wetland soils (Mitsch and Gosselink, 2000). Other factors that might influence the sulfate concentration during the experiments include adsorption, complexation, or precipitation. Because pH values greater than 5 have been found to inhibit sulfate adsorption onto soils (Parfitt, 1978; Ajwa and Tabatabai, 1995) and the pH of mesocosm waters during this study were greater than 7, it is thought that particle adsorption was not important. Additionally, the calculated solubility product for SO_4^{2-} during the manipulations was not exceeded.

Addition of NO_3^- to increase concentrations from 0.1 to 10 mg L^{-1} had no effect on MeHg output. No response in methylation rate to direct addition of NO_3^- (6.2 mg L^{-1}) and phosphate (0.8 mg L^{-1}) was observed by Gilmour et al. (1998). In contrast, Steffan et al. (1988) observed complete inhibition of methylation in sediments due to a NO_3^- concentration increase from 25 to 375 mg L^{-1} . Nitrate amendments in our study were considerably lower (10 mg L^{-1}) than those applied by Steffan et al. (1988) and most likely were not high enough to produce an inhibition of sulfate reduction given the high sulfate concentrations in influent waters.

CONCLUSIONS

Based on this study, in highly managed western watersheds with Hg contamination where water supply may fluctuate significantly, drying and wetting of wetlands could result in resuspension of particulate-bound MeHg, exacerbation of MeHg releases above that measured during times of continuous flow, and pulses of Hg released to downstream systems. Changes in HRT which are common in managed watersheds did not result in changes in MeHg outputs. Sulfate consumption within the mesocosms was found to be an important parameter associated with MeHg output; however, increasing the sulfate concentration of the inlet waters above the high concentrations already present did not result in an immediate change in output. Sulfate concentrations in both influent water sources for the experimental mesocosms were high relative to the average for North American river systems (20 mg L^{-1} ; Livingstone, 1963) and above the optimum range for MeHg production. Sulfate concentrations in arid western U.S. watersheds may be affected by dissolution of gypsum or caliche in desert soils with irrigated agriculture or land use, acid mine drainage, treated wastewater inputs, and atmospheric deposition associated with anthropogenic sources such as coal-fired power plants and ore processing facilities (Zielinski et al., 2001; Turka et al., 2001; Fenn et al., 2003; Kester et al., 2003). In this study the influence of the manipulations on MeHg output of the systems may not reflect MeHg production in the sediments, for actual methylation and demethylation rates were not measured.

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